

case of KBr:Ba the resonance lines disappear when the magnetic field is  $18^\circ$  off the  $[100]$  direction and with KBr:Ca cannot be observed even when the magnetic field is parallel to the  $[100]$  direction. It will be noticed in the spectrum of KBr:Sr (Fig. 3) that only lines from centers oriented parallel to the magnetic field are sufficiently narrow to be clearly visible.

In the parallel orientation, the  $\text{Cl}_2^-$  and  $\text{Br}_2^-$  linewidths are 9.0 and 12.0 gauss, respectively, as compared with 1.3 and 2.5 gauss for the  $\langle 110 \rangle$  oriented centers. Considerations based on dipole-dipole interactions with nuclei of the surrounding ions suggest linewidths of 0.5 and 1.0 gauss, respectively. It has already been shown by Hayes,<sup>11</sup> that in the case of the  $\langle 110 \rangle$  oriented  $\text{Cl}_2^-$  center that part of the linewidth arises from interaction with the nuclei of nearest neighbor ions through weak covalency. This effect, the strained nature of the crystals and the misalignment of the centers may well account for the large linewidth in the present case.

<sup>11</sup> W. Hayes (unpublished).

The ultraviolet optical absorption band of the  $X_2^-$  center in both KCl and KBr occur at shorter wavelength than the bands of the corresponding  $\langle 110 \rangle$  oriented centers. (A detailed discussion of the optical spectra of the  $\langle 110 \rangle$  oriented  $\text{F}_2^-$ ,  $\text{Cl}_2^-$ ,  $\text{Br}_2^-$ , and  $\text{I}_2^-$  is being prepared by Delbecq, Hayes, and Yuster.<sup>4</sup>) This effect is expected to arise largely from the influence of the environment on the excited level of the transition. The effect of environment on the ground state in which paramagnetic resonance is observed should be less and only slight differences in the parameters of the resonance spectra from the two types of center are observed.

#### ACKNOWLEDGMENTS

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## Photoconductivity of Cuprous Oxide in Relation to Its Other Semiconducting Properties\*†

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It is shown that at least two of the three known peaks in the photoconductivity *versus* wavelength curve of  $\text{Cu}_2\text{O}$  are strongly dependent on the oxygen content of the material. The peak near  $600 \text{ m}\mu$  can be shifted from shorter to longer wavelengths by exposing the sample to relatively low oxygen pressures at  $860^\circ\text{C}$ . The peak near  $800 \text{ m}\mu$  is found to increase in magnitude relative to the others under these circumstances. This is in apparent contrast to the results of previous investigators. It is further shown that both results are consistent with the values of the high temperature activation energy of the conductivity process, as well as with the change in bandgap as a function of temperature as obtained from optical absorption measurements under the assumption that  $\text{Cu}_2\text{O}$  can be classified as a nonpolar semiconductor.

#### INTRODUCTION

THE photoconductivity of  $\text{Cu}_2\text{O}$  was first observed by Pfund<sup>1</sup> in 1916 and has since been the subject of considerable investigation.<sup>2-7</sup> The present study is an

outgrowth of research into the cathodoluminescence<sup>8</sup> of  $\text{Cu}_2\text{O}$  and its relation to the other semiconducting properties of this material.

In general the work on  $\text{Cu}_2\text{O}$  can be divided into two categories. Much work is done on the type of  $\text{Cu}_2\text{O}$  used in rectifiers, where often oxygen in excess of the stoichiometric proportions is deliberately introduced. Other work is done on this material for the purpose of measuring the properties of  $\text{Cu}_2\text{O}$  in which the excess oxygen content is kept at a minimum. In the literature this distinction has only recently been emphasized in the work by Anderson and Greenwood<sup>9</sup> and by Böttger<sup>10</sup> in regard to the dark conductivity, and in the work by

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<sup>1</sup> A. H. Pfund, Phys. Rev. **7**, 289 (1916).

<sup>2</sup> W. W. Coblenz, U. S. Bureau Standards Sci. Papers **18**, 603 (1922).

<sup>3</sup> V. P. Barton, Phys. Rev. **23**, 337 (1924).

<sup>4</sup> B. Schönwald, Ann. phys. **15**, 395 (1932).

<sup>5</sup> A. W. Joffe and A. Th. Joffe, Physik. Z. Sowjetunion **11**, 241 (1937).

<sup>6</sup> T. Okada and R. Uno, J. Phys. Soc. Japan **4**, 351 (1949).

<sup>7</sup> G. F. J. Garlick, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 377.

<sup>8</sup> R. Frerichs and F. L. Weichman, J. Appl. Phys. **29**, 710 (1958).

<sup>9</sup> J. S. Anderson and N. N. Greenwood, Proc. Roy. Soc. (London) **A215**, 353 (1952).

<sup>10</sup> O. Böttger, Ann. phys. **10**, 232 (1952).

Bloem<sup>11</sup> on the luminescence. Thus, while previously the value of the activation energy for the conduction process was generally accepted as 0.72 eV,<sup>12</sup> Anderson and Greenwood found the value of 1.05 eV for samples containing a minimum of excess oxygen. Böttger,<sup>10</sup> who measured the activation energy for the conduction process at 900°C as a function of oxygen pressure (down to  $10^{-5}$  mm Hg), also found activation energies higher than the previously accepted values when the oxygen pressure was lowered to less than  $10^{-4}$  mm Hg. In addition he found the time necessary for the sample to reach an equilibrium was quite short at the temperature and oxygen pressures studied.

Thus the early ac photoconductivity measurements made by Schönwald belong in the first of the two categories, since the material used was prepared by oxidizing copper in air at 950°C with subsequent cooling to room temperature in open air. The surface layer of CuO formed by this treatment was removed mechanically or chemically, but the oxygen content of the remaining material must unavoidably have been high. More recently the measurements of Okada and Uno<sup>6</sup> have shown that the relationship between the oxygen content and the photoconductivity is very pronounced. They find that heating the sample under O<sub>2</sub> atmosphere enhances the photoconductive response, in particular near 600 mμ. Vacuum treatment (defined by  $10^{-3}$  mm Hg at 900°C), enhanced the 800 mμ response at the expense of the 600 mμ response. At the same time the sample resistance increased by two orders of magnitude.

In view of the work of Böttger, who showed that the higher value of the activation energy of Cu<sub>2</sub>O cannot be obtained if the O<sub>2</sub> pressure is greater than  $10^{-4}$  mm Hg at 900°C, we must also class the work of Okada and Uno in the first category: that of Cu<sub>2</sub>O containing considerable excess oxygen.

#### EXPERIMENTAL

In order to obtain nearly stoichiometric Cu<sub>2</sub>O we prepared our samples in a vacuum furnace. A Cu foil (Johnson, Matthey, and Company, spectrographically standardized) was completely oxidized in air at about 1050°C, annealed for half an hour at this temperature in high vacuum, and subsequently slowly cooled to room temperature. This procedure was described in the paper by Frerichs and Weichman.<sup>8</sup> The samples had a shiny surface and good translucency to red light; they were 15 mm long, 8 mm wide, and 0.2 mm thick. Two parallel electrodes, 1 mm apart and parallel to the longer dimension of the sample, were made by cathodic sputtering of platinum in an argon atmosphere. For some measurements at elevated temperatures thin platinum wires were spotwelded to the copper foil before

oxidation; this procedure provided good ohmic contacts to the Cu<sub>2</sub>O at all temperatures.

For the measurements above as well as below room temperature the sample was sealed into an evacuated container. The vacuum was maintained by a side tube filled with charcoal and immersed in liquid nitrogen.

A Beckman quartz spectrophotometer with tungsten lamp provided the monochromatic radiation for the photoconductivity measurements. The energy output of the monochromator between 500 and 2000 mμ was calibrated with a Moll and Burger E5 standard thermopile. The monochromatic radiation after having been chopped at 1080 cycles per second at the exit slit of the monochromator was focused on the sample on the space between the two electrodes.

The photoconductivity defined as  $(i_{\text{light}} - i_{\text{dark}})/i_{\text{dark}}$  was measured with a high gain tuned amplifier. The input impedance of the amplifier was matched to the dark resistance of the sample, which varied from  $10^4 \Omega$  at 490°C to more than  $2 \times 10^7 \Omega$  at room temperature. Additional measurements were made with sensitive dc instruments at a sample temperature of  $-100^\circ\text{C}$ . At this temperature the dark resistance was greater than  $10^{12} \Omega$ .

#### RESULTS

Conductivity measurements on a number of samples from 1060°C down to  $-80^\circ\text{C}$  were used to establish the character of the material under the experimental procedure used [Fig. (1)]. The Cu<sub>2</sub>O samples were found to be similar to those described by Anderson and Greenwood, having high temperature activation energies varying from 0.90 to 1.05 eV and the characteristic kink in the conductivity curve at 350°C. Two additional kinks were found near 80°C and  $-65^\circ\text{C}$ . They are probably identical to those mentioned by Vogt<sup>13</sup> and Blankenburg and Schubart.<sup>14</sup>

Furthermore the position of the absorption edge was measured over the wide range of 2°K to 1100°K [Fig. (2)]. It was defined as the wavelength at which the transmission dropped to one-half of its value at the relatively flat portion of the curve immediately preceding the sharp drop. The edge shifts by  $6.5 \times 10^{-4}$  eV per °K between room temperature and 1100°K. This value is in close agreement with the older value of 0.17 mμ per degree found by Mönch<sup>15</sup> between 225 and 575°K.

Measurements of the photoconductivity of the samples were then made. They covered as wide a range of temperatures as was feasible. According to these measurements the photoconductive response as a function of the incident wavelength is far more sensitive to atmospheric oxygen than the optical absorption. Freshly made samples had, at room temperature, a very high resist-

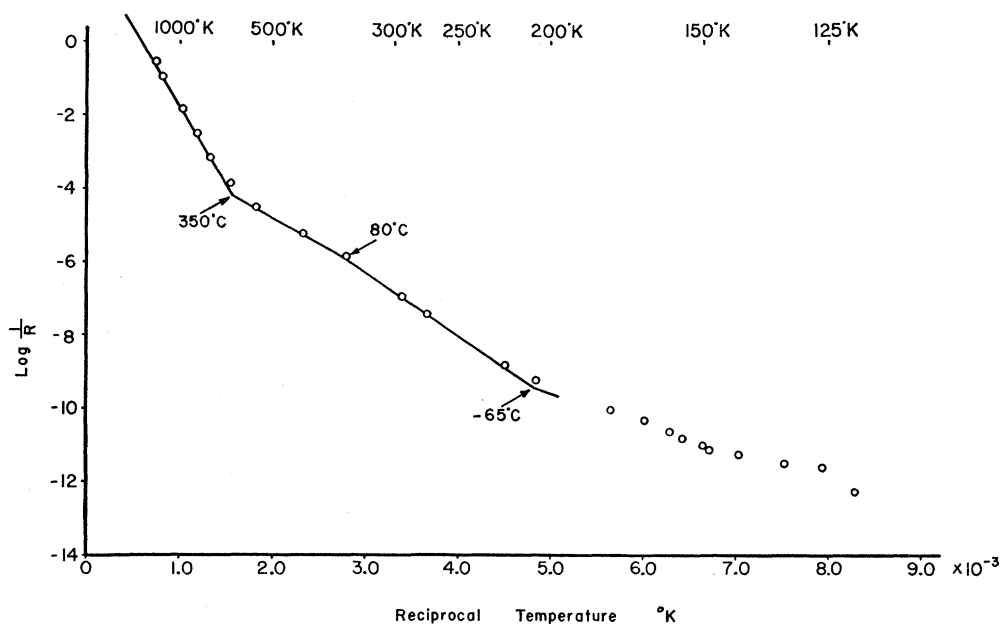
<sup>11</sup> J. Bloem, Philips Research Repts. **13**, 167 (1958).

<sup>12</sup> W. Jusé and B. W. Kurtschatow, Physik. Z. Sowjetunion **2**, 453 (1932).

<sup>13</sup> W. Vogt, Ann. phys. **7**, 183 (1930).

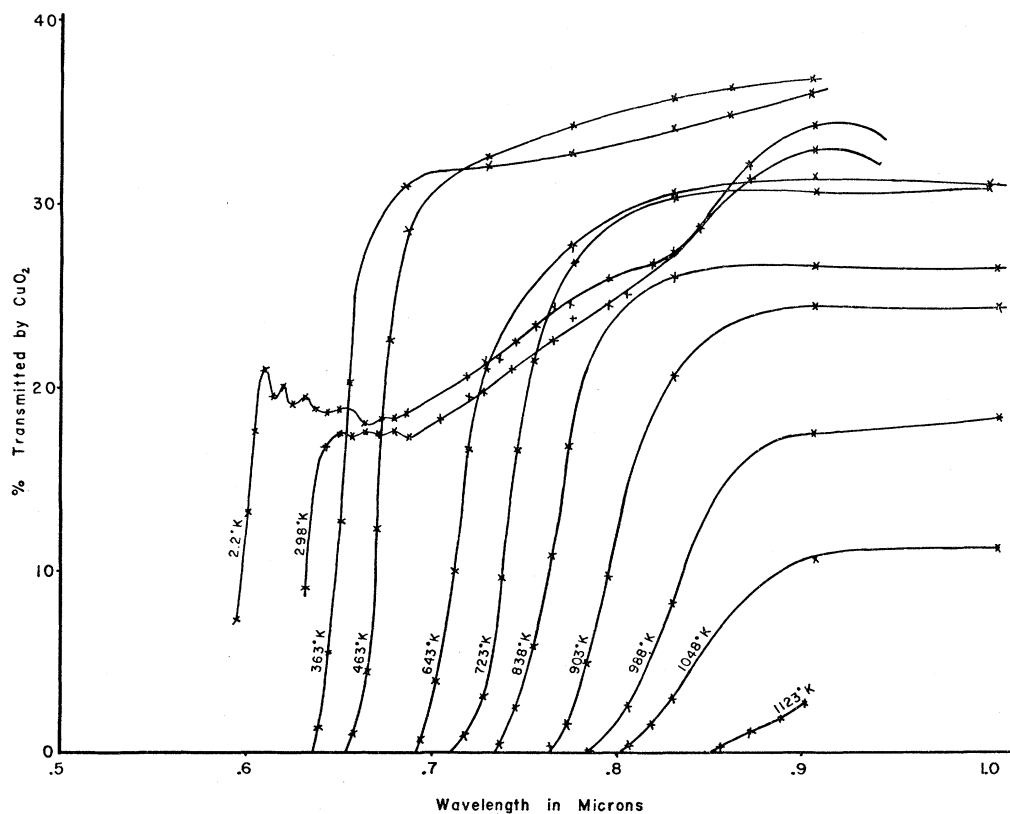
<sup>14</sup> G. Blankenburg and G. Schubart, Ann. phys. **12**, 281 (1953).

<sup>15</sup> G. Mönch, Z. Physik **78**, 728 (1932).

FIG. 1. Conductivity of  $\text{Cu}_2\text{O}$  in vacuo as a function of temperature.

ance ( $2 \times 10^7 \Omega$  or higher) with three regions of photo-sensitivity: the first region around  $600 \text{ m}\mu$ , a second near  $800 \text{ m}\mu$ , and a third region near  $1100 \text{ m}\mu$ . This

corresponds to the measurements of Garlick.<sup>7</sup> After some weeks of exposure to the atmosphere the resistance dropped by a few orders of magnitude; at the same time,

FIG. 2. Optical transmission of  $\text{Cu}_2\text{O}$  as a function of incident wavelength for various temperatures.

the response to the first two spectral regions was greatly increased.

To test the dependence of the photoconductive response on oxygen content, a number of samples were given various degrees of outgassing at high temperatures. Figure (3) shows four curves of photoconductive response as a function of wavelength of the same sample. The scale is arbitrarily adjusted to give the same ordinate at 500  $m\mu$  for each curve. The Moss relationship<sup>16</sup> between the bandgap and the decrease in photoresponse toward longer wavelengths suggests the use of the wavelength at which the response drops to one-half of its maximum value ( $\lambda_i$ ) as the parameter by which to describe the experimental results. Curve (A) shows the response of the sample after having been exposed to the atmosphere for a few weeks. The value for  $\lambda_i$  is 638  $m\mu$ , while the dark resistance is  $3 \times 10^5 \Omega$ . After this set of measurements the sample was sealed in a quartz tube and heated to 860°C in a vacuum obtained by a charcoal trap surrounded by liquid nitrogen. After outgassing under these conditions for one hour, the sample was rapidly quenched to room temperature by pouring cold water on the evacuated quartz tube. Curve (B) shows the response obtained immediately after removal from the quartz tube. The dark resistance remained at  $3 \times 10^5 \Omega$ , but  $\lambda_i$  shifted to 577  $m\mu$ . Curve (C) shows the spectral response of this same sample after a second vacuum treatment at 860°C, after which the sample was not quenched but cooled slowly in vacuum to room temperature. The resistance of the sample increased to  $2.2 \times 10^7 \Omega$ , but the spectral response changed only very slightly. The  $\lambda_i$  value shifted to 586  $m\mu$ . Finally Curve (D) shows the response obtained by a third heat treatment. The sample was heated to 860°C under the vacuum obtained from a mechanical pump ( $10^{-2}$  to  $10^{-3}$  mm Hg). The charcoal trap was cooled with liquid nitrogen after the oven had already been turned off in order to limit the oxygen intake at lower temperatures. The  $\lambda_i$  value again moved to longer wavelengths, i.e., 616  $m\mu$ , while the dark resistance dropped from the previous value of  $2.2 \times 10^7 \Omega$  to  $2 \times 10^6 \Omega$ .

The figure furthermore shows the following significant result. Even though the dark resistance of the sample in curve (B) is two orders of magnitude less than in curve (C), the same relative magnitudes of the 600  $m\mu$  and 800  $m\mu$  responses are found, with a drop in sensitivity from the visible to the infrared wavelengths of a factor of 500. In curve (D) the drop in sensitivity is still present, but is reduced to only a factor of 125. Other samples, of greater oxygen content, as in (A) show only a 10-fold drop in sensitivity from the visible to the infrared. Samples checked under similar atmospheric treatments also showed the reversibility of  $\lambda_i$  values.

<sup>16</sup> T. S. Moss, *Photoconductivity in the Elements* (Academic Press, New York, 1952).

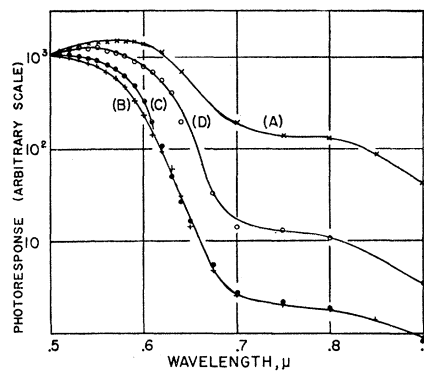


FIG. 3. Photoconductive response of  $\text{Cu}_2\text{O}$  of varying oxygen content as a function of the incident wavelength.

### DISCUSSION

Our experiments confirm the work of Anderson and Greenwood in establishing the higher value of the activation energy in the conduction process: 1 ev at temperatures above 350°C. Assuming this to be the intrinsic range and  $\text{Cu}_2\text{O}$  to be a nonpolar semiconductor, we arrive at a bandgap value slightly above 2 ev at room temperature. The bandgap as determined from the Moss relation lies between 1.94 ev, as obtained from a slightly deteriorated sample, and 2.14 ev, as obtained after vacuum annealing. The optical transmission measurements, which gave an absorption edge at 640  $m\mu$  would ordinarily indicate an "optical" bandgap of 1.94 ev. For  $\text{Cu}_2\text{O}$  this cannot be true because of the existence of the exciton structure at wavelengths shorter than 640  $m\mu$ .<sup>17-19</sup> The series limit of the most energetic exciton levels, which should be the bandgap, was found to be 2.04 ev<sup>25</sup> at room temperature, which agrees closely with the conductivity and photoconductivity values mentioned above. Thus, contrary to the suggestion of Okado and Uno, the 800  $m\mu$  maximum in the photoconductivity should be due to higher rather than lower oxygen content, or else to a more "efficient" distribution of the oxygen "impurity."

Thus we see that the optical and electrical properties yield close to the same value for the bandgap, if one assumes  $\text{Cu}_2\text{O}$  to be a nonpolar semiconductor. We will now discuss some of the other implications of this assumption.

In theoretical work on the temperature dependence of the bandgap of a semiconductor, the distinction between polar and nonpolar semiconductors is great. For polar crystals the temperature dependence was given by Radkowsky<sup>20</sup> and later extended by Fan<sup>21</sup> and Muto and

<sup>17</sup> T. F. Gross and N. A. Karayev, *Doklady Akad. Nauk. U.S.S.R.* 84, 261, 471 (1952).

<sup>18</sup> S. Nikitine, L. Couture, M. Sieskind, and G. Perny, *Compt. rend.* 238, 1786 (1954); *J. phys. radium* 16, 415 (1955).

<sup>19</sup> J. H. Apfel and L. N. Hadley, *Phys. Rev.* 100, 1689 (1955).

<sup>20</sup> A. Radkowsky, *Phys. Rev.* 73, 749 (1948).

<sup>21</sup> H. Y. Fan, *Phys. Rev.* 82, 900 (1951).

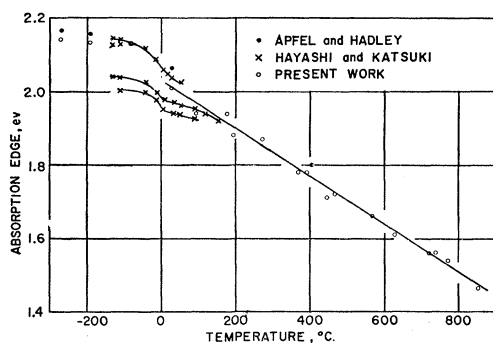


Fig. 4. Absorption edge of  $\text{Cu}_2\text{O}$  as a function of temperature.

Oyama.<sup>22</sup> Fan and Muto and Oyama gave in addition the results to be expected for nonpolar crystals. In contrast to a polar crystal, which theoretically should show a change in bandgap  $\Delta E$  proportional to  $(1 - \exp(h\nu/kT))^{-1}$ , nonpolar crystals, according to the calculations of Muto and Oyama, should show three distinct regions:

For temperatures large compared with the Debye temperature  $\theta$ ,  $\Delta E$  is directly proportional to the absolute temperature  $T$ ;

For  $T \ll \theta$ , the temperature dependence of the change in bandgap should be  $\Delta E$  proportional to  $T^2 - (bT - T^2) \exp(-b/T)$ ;

For a value of  $T$  close to that of  $\theta$ , the behavior is transitional.

The Debye temperature of  $\text{Cu}_2\text{O}$  was first estimated to be at  $280^\circ\text{K}$  by Fröhlich and Mott<sup>23</sup> from the temperature dependence of the mobility and the near free path of positive holes. Thermal conductivity measurements by Fritts<sup>24</sup> confirmed this value.

Thus, the experimental work at  $T \gg \theta$  points rather conclusively to a linear relationship between  $\Delta E$  and  $T$ , judging from the results of Mönch, Hayashi and Katsuki<sup>25</sup> and our own work. For  $T \ll \theta$  the work of Nikitine *et al.* and Apfel and Hadley shows a quadratic

temperature dependence of  $\Delta E$ . For the region between  $-100^\circ\text{C}$  and  $+100^\circ\text{C}$  Hayashi and Katsuki have published a set of curves of the position of the series limits of the excitons, showing a rather abrupt transition from quadratic to linear temperature dependence. We have collected the experimental curves of Apfel and Hadley, Hayashi and Katsuki, and of our own in Fig. 4.

Finally, it should be mentioned that the static dielectric constant for nonpolar crystals is equal to the high frequency dielectric constant, whereas for polar crystals the static value is higher than the value determined at optical frequencies. From measurements of the index of refraction the high frequency dielectric constant appears to be well established at about 7.5.<sup>7</sup> The static dielectric constant as determined from  $\text{Cu}_2\text{O}$  powders has been variously stated as being 12<sup>26</sup> and 10.5.<sup>27</sup> We believe more credence can be given to the measurements on the solid material, giving a value of  $7.0 \pm 0.6$  as determined by Völkl<sup>28</sup> and more recently a value of  $6.9 \pm 0.3$  as determined by Rau at microwave frequencies.<sup>29</sup>

## CONCLUSION

It was shown that the photoconductive response of cuprous oxide containing a minimum of excess oxygen allows us to calculate the same bandgap as is obtained from high temperature conductivity measurements, without taking into account any difference which might exist between the static and high frequency dielectric constant. It was further shown that this is in good agreement with the temperature dependence of the optical transmission measurements, which are typical of nonpolar semiconductors, and recent measurements of the static dielectric constant.

## ACKNOWLEDGMENTS

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<sup>22</sup> T. Muto and S. Oyama, Progr. Theoret. Phys. (Kyoto) **5**, 833 (1950).

<sup>23</sup> H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **171**, 496 (1939).

<sup>24</sup> R. B. Fritts, Northwestern University dissertation (unpublished).

<sup>25</sup> M. Hayashi and K. Katsuki, J. Phys. Soc. Japan **7**, 599 (1952).

<sup>26</sup> K. Højendahl, Z. physik. Chem. **B20**, 54 (1933).

<sup>27</sup> A. Guntherschulz and F. Keller, Z. Physik **75**, 78 (1932).

<sup>28</sup> A. Völkl, Ann. phys. **14**, 210 (1932).

<sup>29</sup> R. R. Rau, University of Pennsylvania dissertation (unpublished).